

GREEN COMPACT AND PROCESS FOR COMPACTING THE SAME,  
METALLIC SINTERED BODY AND PROCESS FOR PRODUCING THE SAME,  
WORKED COMPONENT PART  
AND  
METHOD OF WORKING

Field of the Invention

**【0001】** The present invention relates to a high-density green compact comprising a raw material powder whose major component is an active metallic element such as Ti and Al (hereinafter referred to as an active metallic powder wherever appropriate), a process for compacting the same, a high-density metallic sintered body which is made by sintering the green compact, and a process for producing the same.

**【0002】** Moreover, the present invention relates to a worked component part which is made by working a metallic workpiece whose major component is an active metallic element, and a method of working the same.

Description of the Related Art

**【0003】** In order to reduce the manufacturing cost of component parts by reducing the expensive working cost, or in order to obtain characteristics which are not available in bulky cast materials, green compacts which are formed by pressurizing raw material powders have been used conventionally. The green compacts are often turned into sintered bodies subsequently, but are used as they are like powder magnetic cores.

**【0004】** In order to utilize the characteristics of green compacts, green compacts are required to have a high density in most cases. In order to produce high-density green compacts, it is inevitable

to form raw material powders by pressuring by high pressures. Usually, however, the higher the compacting pressure is, the larger the frictional force between the raw material powders and dies is. As a result, when raw materials are formed by pressuring by large pressures, it has become difficult to eject the resulting green compacts from the dies. Moreover, galling and the like occur to damage the dies when ejecting the green compacts, or the surface of the green compacts is roughened.

**【0005】** It is possible, of course, to think of improving the drawbacks by using lubricants in a large amount. However, such a measure might eventually result in lowering the density of green compacts. Moreover, the lubrication increases the working cost because it is required to carry out a degreasing or dewaxing step after the pressure compacting step.

**【0006】** Under the circumstances, there have been proposed a large number of processes for efficiently producing high-density green compacts. In the proposed processes, the type of lubricants, the lubrication methods, the compacting temperatures are tried out variously. For example, the following publications disclose the relevant matters: Japanese Unexamined Patent Publication (KOKAI) No. 62-109,902, Japanese Unexamined Patent Publication (KOKAI) No. 62-294,102, Japanese Unexamined Patent Publication (KOKAI) No. 5-271,709, Japanese Unexamined Patent Publication (KOKAI) No. 8-100,203, Japanese Unexamined Patent Publication (KOKAI) No. 9-104,902, Japanese Unexamined Patent Publication (KOKAI) No. 11-193,404, Japanese Unexamined Patent Publication (KOKAI) No. 11-100,602, Japanese Unexamined Patent Publication (KOKAI) No. 11-140,505, Japanese Unexamined Patent Publication (KOKAI) No.

2000-273,502, Japanese Unexamined Patent Publication (KOKAI) No. 2000-290,703, Japanese Unexamined Patent Publication (KOKAI) No. 2001-294,902, PCT International Laid-Open Publication No. WO98/41,347, United States Patent No. 4,955,798, and a research paper "INFLUENCE OF TEMPERATURE ON PROPERTIES OF LITHIUM STEARATE LUBRICANT (Powder Metallurgy & Particulate Materials, vol. 1, 1997)." However, it is improper for all such proposals to produce high-density green compacts at reduced cost.

**[0007]** Hence, the inventors of the present invention developed first in the world a process for producing a high-density green compact whose density is very close to the true density by remarkably high compacting pressures which have not been available conventionally while securing the longevity and the like of dies. PCT International Laid-Open Publication No. WO01/43,900 discloses the details.

**[0008]** However, when the aforementioned publications as well as the descriptions of PCT International Laid-Open Publication No. WO01/43,900 are examined, it is seen that the raw material powders comprise iron powders or iron alloy powders in most of the green-compact production processes proposed so far. Namely, no actual proposals have been ever made on how to form raw material powders whose major component is an active metallic element such as Ti and Al into green compacts.

**[0009]** As far as the present inventors know at present, they have not found out any processes at all in which raw materials are formed by high pressures, not by means of internal or admixing lubrication methods, but by means of die wall lubrication methods at industrial or mass-production level at least.

**【0010】** The fact does not mean that demands are less for green compacts whose raw material powder comprises Ti or Al. Demands for such green compacts are rather high because it has been required recently to make a diversity of component parts lightweight. In particular, in the case of component parts made of pure titanium or titanium alloys which are difficult to work, when a powder compacting process is used, there arises a great merit in that it is possible to reduce the cost by near-net or net shaping.

**【0011】** However, it has been the technical common knowledge that it is impossible to form raw material powders comprising an active metallic element such as Ti and Al by high pressures at industrial level. This is because galling occurs on the inner surface of dies instantaneously or the inner surface of dies is roughened when such high-pressure compacting is carried out. Moreover, it is because the resulting green compacts cannot be ejected from dies. In addition, very expensive dies cannot be used even after one and only high-pressure compacting operation so that a great loss might arise.

**【0012】** Due to the circumstances, when raw material powders comprising an active metallic element are formed by pressurizing, it is not possible to heighten the compacting pressures. Accordingly, the resulting green compacts naturally have a low attainable density. For example, when green compacts comprise a Ti powder, the green compacts have a density which is only 80% or less of the true density.

**【0013】** Moreover, when Ti powders are formed conventionally by pressuring by means of an internal lubrication method, a dewaxing step is required additionally before the resulting green compacts are sintered in vacuum. In addition, since the major components

of the lubricants used in this instance, such as hydrogen, nitrogen and carbon, are likely solve in Ti, internal lubrication methods are unpreferable.

**【0014】** In order to avoid using such lubricants, CIP (i.e., cold isostatic press) forming and RIP (i.e., rubber isostatic press) forming in which rubber molds are used. However, even when such forming methods are employed, it is not possible to carry out high-pressure compacting sufficiently. Moreover, the facilities are very large and expensive. In addition, the resulting green compacts exhibit low dimensional accuracy. Thus, net-shaped component parts, the greatest characteristic of green compacts, have not been produced yet actually.

**【0015】** The situations are the same for the case where Al powders are used. Moreover, when Al powders are mixed with lubricants and are formed thereafter, there arises another problem that it is impossible to dewax sufficiently because the dewaxing temperature of the lubricants is close to 500 °C approximately, the sintering temperature of the resulting green compacts.

#### SUMMARY OF THE INVENTION

**【0016】** The present invention has been developed in view of such circumstances. It is therefore an object of the present invention to provide a process for compacting a green compact with a raw material powder whose major component is an active metallic element such as Ti and Al, and which makes it possible to form the raw material powder by high pressures at actual level, and to provide high-density green compacts produced thereby.

**【0017】** Moreover, it is a further object of the present invention to provide metallic sintered bodies which are made by sintering the

green compacts, and a process for producing the same.

**【0018】** In addition, not limited to the process for compacting a green compact and the like, it is a furthermore object of the present invention to provide a method of working a metallic workpiece whose major component is an active metallic element, and worked component parts produced thereby.

**【0019】** Hence, the present inventors studied wholeheartedly in order to solve the problems, and repeated trials and errors. As a result, they thought of applying warm compaction to raw material powders whose major component is an active metallic element (hereinafter simply referred to as an "active metallic powder" wherever appropriate) by means of a die wall lubrication, and actually confirmed advantages resulting therefrom. Thus, they arrived at completing the present invention.

(Process for Compacting Green Compact)

**【0020】** A process for producing a green compact according to the present invention comprises the steps of:

applying a higher fatty acid-based lubricant to an inner surface of a die;

filling a raw material powder whose major component is an active metallic element into the die;

compacting the raw material powder by warm pressurizing, thereby making a green compact; and

ejecting the green compact from the die;

whereby the resulting green compact has a high density.

**【0021】** In accordance with the present compacting process, even when active metallic powders are used, it is possible to produce high-density green compacts by high-pressure compacting. In this

instance, no galling and the like occur on the inner surface of dies substantially, and accordingly it is possible to produce green compacts with favorable dimensional stability and superficial roughness. Therefore, the longevity of dies is extended, the yield of raw material powders is improved, and the working cost is reduced by near net shaping. Thus, it is possible to sharply reduce the cost of green compacts as well as sintered bodies made therefrom.

**【0022】** Moreover, in accordance with the present compacting process, it is possible to produce advantages satisfactorily, not by lubricating raw materials internally, but by simply lubricating dies. Accordingly, the using amount of lubricants is less. Further, it is possible to highly densify green compacts, and it is simultaneously possible to obviate dewaxing steps before green compacts are sintered. Furthermore, it is possible to inhibit lubricants from adversely affecting green compacts.

**【0023】** In addition, in accordance with the present compacting process, the ejection forces can be reduced sharply compared with those in conventional compacting processes, though the compacting pressures are enlarged remarkably. Accordingly, it is possible to eject green compacts with ease. Consequently, it is possible to greatly enhance the production efficiency of green compacts.

**【 0024 】** By the way, the present inventors are currently investigating wholeheartedly the reasons why it is possible to form active metallic powders by high pressures, which person having ordinary skill in the art has been considering impossible. The reasons can be believed as follows. A new metallic soap film, which is different from the higher fatty acid-based lubricant used for lubricating the die, is formed between the green compact and the

inner surface of the die to sharply reduce the friction coefficient therebetween. Moreover, it is also possible to believe that the higher fatty acid-based lubricant adsorbs to the surface of the green compact to produce the Rebinder effect. In addition, it is also possible to believe that it results from a super-lubricative action which is beyond the conventional recognition so far. However, according to the recent examinations and studies by the present inventors, it is believed reasonable that it results from the fact that the metallic soap film is formed newly on the surface of the green compact in the compacting step. Namely, the compacting step is believed to be a step in which a new metallic soap film, which comprises the active metallic element and is different from the higher fatty acid-based lubricant, is formed on the surface of the green compact. For example, when the active metallic element is Ti, the metallic soap film is believed to comprise Ti salts of higher fatty acids. When the active metallic element is Al, the metallic soap film is believed to comprise Al salts of higher fatty acids.

**[0025]** It is apparent anyway that the frictional force between the raw material powder or green compact and the die is reduced sharply because the ejection force is very low. However, it is not directly related to the fact that the friction coefficient is low exceptionally. Depending on the types of the raw material powder, there are green compacts whose expansion (or spring back magnitude) is less after they are ejected from the die. In this instance, even if the friction coefficient is not low exceptionally, the frictional force is reduced when the green compact is ejected from the die.

**[0026]** The active metallic element set forth in the present specification can be Ti, Al, Mg, Zr, Na, and rare-earth elements



such as La and Ce. Ti, Al, Mg are important as actual metallic materials. Namely, it is particularly important industrially when the raw material powder comprises Ti, Al or Mg. The details will be described later. Note that the "raw material powder whose major component is an active metallic element" set forth in the present specification means that the raw material powder comprises the objective specific active element in an amount of 50 atomic % or more when the entire raw material powder is taken as 100 atomic %. The raw material powder can be not only metallic powders but also ceramic powders. Therefore, the resulting green compact can be not only formed metallic bodies but also formed ceramic bodies.

(Green Compact)

**【0027】** The present invention is not limited to the present compacting process, and can be grasped as a green compact produced as a result of the present production process.

**【0028】** For example, on the assumption that a green compact is produced by the present compacting process, the present invention can be adapted to a green compact wherein the active metallic element is Ti; and a green density being an apparent density of the green compact is 85% or more of a true density determined by a composition of the raw material powder.

**【0029】** In this instance, the green density can be 88% or more, 90% or more, 95% or more and even 98% or more of the true density by controlling the compacting pressure. It is even possible to approach the green density 100%, the upper limit, limitlessly.

**【0030】** Likewise, on the assumption that a green compact is produced by the present compacting process, the present invention can be adapted to a green compact wherein the active metallic element is

Al; and a green density being an apparent density of the green compact is 90% or more of a true density determined by a composition of the raw material powder.

**【0031】** In this instance as well, the green density can be 93% or more, 95% or more and even 98% or more of the true density by controlling the compacting pressure. It is even possible to approach the green density 100%, the upper limit, limitlessly.

**【0032】** In the case of conventional green compacts comprising Ti powders, the green density is about 80% of the true density at the highest. In the case of conventional green compacts comprising Al powders, the green density is about 85% of the true density at the highest. Based on these facts, it is amazing precisely that the present green compacts have such a high density. Of course, even when such high-density green compacts are produced, in accordance with the present compacting process, no galling and the like occur to the die, the ejection force is low, and green compacts with favorable dimensional accuracy and superficial roughness can be obtained as described above.

(Process for Producing Metallic Sintered Body)

**【0033】** The present invention is not limited to the present compacting process, and can be grasped as a process for producing a metallic sintered body which is made by sintering the green compact produced by the present compacting process.

**【0034】** The present invention can be adapted to a process for producing a metallic sintered body comprising the steps of:

applying a higher fatty acid-based lubricant to an inner surface of a die;

filling a raw material powder whose major component is an

active metallic element into the die;

compacting the raw material powder by warm pressurizing, thereby making a green compact;

ejecting the green compact from the die; and

sintering the green compact by heating, thereby making a metallic sintered body;

whereby the resulting metallic sintered body has a high density.

**【0035】** In accordance with the present production process, it is possible to produce high-density metallic sintered bodies with ease. Moreover, since the amount of lubricants used in compacting the green compact is extremely less, no dewaxing step is required in the following sintering step so that the sintering step can be simplified remarkably. As a result, the production cost can be reduced accordingly so that it is possible to produce high-density metallic sintered bodies at much lower cost.

(Metallic Sintered Body)

**【0036】** Moreover, the present can be grasped as a metallic sintered body produced by the present production process.

**【0037】** For example, on the assumption that a metallic sintered body is produced by the present production process, the present invention can be adapted to a metallic sintered body wherein the active metallic element is Ti; and a sintered-body density being an apparent density of the metallic sintered body is 85% or more of a true density determined by a composition of the raw material powder.

**【0038】** In this instance, the greater the green density before sintering is, the greater the sintered-body density is. The sintered-body density can be 90% or more, 95% or more, 97% or more

and even 99% or more of the true density. Thus, the sintered-body density approaches 100%, the upper limit, limitlessly more than the green density does.

**[0039]** Likewise, on the assumption that a metallic sintered body is produced by the present production process, the present invention can be adapted to a metallic sintered body wherein the active metallic element is Al; and a sintered-body density being an apparent density of the metallic sintered body is 90% or more of a true density determined by a composition of the raw material powder.

**[0040]** In this instance as well, the greater the green density before sintering is, the greater the sintered-body density is. The sintered-body density can be 93% or more, 95% or more, 97% or more and even 99% or more of the true density. Thus, the sintered-body density approaches 100%, the upper limit, limitlessly more than the green density does.

**[0041]** In either case, the present metallic sintered bodies suffer less from dimensional variations such as dimensional contractions after sintering, because the green density is large before sintering. Accordingly, although they are sintered products comprising the active metallic element, they can be formed as net shapes. Consequently, it is possible to achieve reducing the cost of Ti or Al products with ease.

(Method of Working and Worked Component Member)

**[0042]** In accordance with the present invention, it is possible to form active metallic powders by high pressures. Based on the fact, a variety of modes according to the present invention have been described so far. However, it is believed that the present invention can be fundamentally characterized in that the frictional

force acts remarkably less between the inner surface of the die and the active metallic powder or the green compact produced by pressurizing it. Therefore, the present invention is not limited to the case where raw material powders are formed by pressuring, and can be naturally applied to the case where physical metallic workpieces are worked into desired shapes.

**【0043】** For example, the present invention can be grasped as a method of working, comprising the steps of:

applying a higher fatty acid-based lubricant to at least one surface selected from the group consisting of a surface of a metallic workpiece whose major component is an active metallic element and a working surface of a die; and

warm working the metallic workpiece with the die.

**【0044】** In accordance with the present working method, even metallic workpieces comprising active metallic powders can be worked into desired shapes not only efficiently and at reduced cost, but also without causing galling and the like between them and the die, in the same manner as the above-described present compacting process.

**【0045】** The "metallic workpiece" set forth in the present specification can not only be cast materials but also sintered materials. The shape of the metallic workpiece is not limited in particular, and accordingly can be ingots, plates and pipes. In short, different from metallic powders, the metallic workpiece can be those having macro contours. Moreover, the term, "working," means that the contour of macro physical workpieces is arranged to desired shapes, specifically, the workpiece is worked into desired shapes.

**【0046】** As for such working, there are forging, rolling, extruding,

drawing, component rolling, coining, sizing and re-compressing. Depending on the types of working, different dies are used. For example, the die can be forging molds, rolls and dies.

**【0047】** In order to carry out the working step in warm states, at least one of the die and the metallic workpiece can be heated before the working step, or can be heated simultaneously with the working step.

**【0048】** Since the metallic workpiece has a contour, the higher fatty acid-based lubricant can be applied to the metallic workpiece in the applying step. Of course, the higher fatty acid-based lubricant can be applied to the die in the same manner as the present compacting process. For example, the applying step can be dipping methods in which the workpiece, which is heated, is immersed into a dispersion, in which the higher fatty acid-based lubricant is dispersed, or spraying methods in which a dispersion, in which the higher fatty acid-based lubricant is dispersed, is sprayed onto the metallic workpiece or the die, which is heated. Note that it is needless to say that the present invention can be grasped as a worked component part produced by the present working method.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**【0049】** A more complete appreciation of the present invention and many of its advantages will be readily obtained as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings and detailed specification, all of which forms a part of the disclosure:

Fig. 1 is a graph for illustrating the relationships between the compacting pressures and the green densities (or relative

densities) when room-temperature and warm compaction were carried out with a pure titanium powder;

Fig. 2 is a graph for illustrating the relationships between the compacting pressures and the ejection forces in the compacting operations;

Fig. 3 is a graph for illustrating the relationships between the compacting pressures applied to the pure titanium powder and the relative densities of the metallic sintered bodies produced by sintering the resulting green compacts;

Fig. 4 is a graph for illustrating the relationships between the compacting pressures applied to the pure titanium powder and the dimensional changes after the green compacts were sintered;

Fig. 5 is a graph for illustrating the relationships between the compacting pressures and the green-compact densities (or relative densities) when warm compaction was carried out with titanium alloy powders;

Fig. 6 is a graph for illustrating the relationships between the compacting pressures and the ejection forces in the compacting operation;

Fig. 7 is a graph for illustrating the relationships between the compacting pressures applied to the titanium alloy powders and the relative densities of the metallic sintered bodies produced by sintering the resulting green compacts;

Fig. 8 is a graph for illustrating the relationships between the compacting pressures and the green densities (or relative densities) when room-temperature and warm compaction were carried out with a pure aluminum powder;

Fig. 9 is a graph for illustrating the relationships between

the compacting pressures and the ejection forces in the compacting operations;

Fig. 10 is a graph for illustrating the relationships between the compacting pressures and the green-compact densities (or relative densities) when room-temperature and warm compaction were carried out with a pure aluminum powder and an aluminum alloy powder;

Fig. 11 is a graph for illustrating the relationships between the compacting pressures and the ejection forces in the compacting operations;

Fig. 12 is a graph for illustrating the relationships between the sintering time and the relative density exhibited by a sintering-resistant material;

Fig. 13 is a graph for illustrating the relationships between the sintering time and the dimensional change exhibited by the sintering-resistant material;

Fig. 14 is a bar graph for comparing the differences of the relative density, tensile strength and elongation between an example and comparative examples when the production conditions were changed;

Fig. 15 is a graph for comparing the differences of the fatigue strength between an example and a comparative example when the production conditions were changed;

Fig. 16 is a secondary ion image when a surface of a green compact comprising a pure Ti powder was observed by TOF-SIMS (i.e., time of flight-secondary ion mass spectrometry); and

Fig. 17 is a secondary ion image when a surface of a green compact comprising a pure Al powder was observed by TOF-SIMS.



#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**【0050】** Having generally described the present invention, a further understanding can be obtained by reference to the specific preferred embodiments which are provided herein for the purpose of illustration only and not intended to limit the scope of the appended claims.

**【0051】** The present invention will be hereinafter described in more detail with reference to specific preferred embodiments. Note that the following descriptions are applicable appropriately to all of the compacting process, green compacts, metallic sintered bodies, process for producing the same, working method and worked component part according to the present invention.

##### (1) Raw Material Powder

**【0052】** As described above, the raw material powder comprises a powder whose major component is an active metallic element. Ti-based powders and Al-based powders are the representative options.

**【0053】** When the active metallic element is Ti, the raw material powder can comprise pure Ti powders, Ti alloy powders and Ti compound powders, for example. The raw material powder can be simple powders comprising one of the powders independently, or can be mixture powders comprising two or more of the powders. In addition to Ti, the raw material powder can further comprise at least one element selected from the group consisting of Al, Zr, Hf, V, Nb, Ta, Sc, Cr, Fe, Mo, Sn, W, Mn, Ni, Cu, Si, C, B, N and O.

**【0054】** Representative Ti compound powders can be titanium boride powders comprising  $TiB_2$ , titanium carbide powders comprising  $TiC$ , titanium nitride powders comprising  $TiN$ , and titanium oxide powders

comprising  $\text{TiO}_2$ , for example.

**【0055】** The included form of the respective elements does not matter at all. For example, the respective elements can be included in the raw material powder as pure powders, alloy powders and compound powders. The usage and characteristics of the green compacts, or the sintered bodies resulting therefrom, and the cost of the powders can determine which elements are included in the raw material powder.

**【0056】** When the active metallic element is Al, the raw material powder can comprise pure Al powders, Al alloy powders and Al compound powders, for example. In addition to Al, the raw material powder can further comprise at least one element selected from the group consisting of Cu, Mn, Zr, Sr, Ni, Cr, Fe, Mo, Sn, Si, C, B, N and O. Note that representative Al compound powders are aluminum oxide powders comprising  $\text{Al}_2\text{O}_3$ .

**【0057】** Similarly to the raw material powder whose major component is Ti, the raw material powder whose major component is Al can be likewise simple powders comprising one of the powders independently, or can be mixture powders comprising two or more of the powders. The included form of the respective elements does not matter at all.

**【0058】** The raw material powder can be mixture powders in which hard-particle powders comprising borides, nitrides, oxides or carbides. In the mixture powders, two or more hard-particle powders can be mixed. When hard particles comprise Ti or Al compounds, the hard-particle powders make the above-described Ti compound powders or Al compound powders.

**【0059】** When the raw material powder including a hard-particle powder is subjected to powder compacting, it is possible to easily produce a composite material in which the hard particles are

dispersed uniformly in the matrix composed of the active metallic element, such as Ti and Al, and the alloys resulting therefrom. Such a composite material is good in terms of the mechanical characteristics, such as the strength, rigidity, heat-resistance and wear-resistance. In particular, the metallic sintered bodies made by sintering the green compacts effect the advantage remarkably.

**【0060】** In addition to  $\text{TiB}_2$ , TiB, TiC, TiN,  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  described above, the hard particles can comprise SiC,  $\text{Si}_2\text{N}_4$ ,  $\text{B}_4\text{C}$ , CrN,  $\text{Cr}_2\text{N}$ , MoB, CrB,  $\text{Y}_2\text{O}_3$ , and  $\text{ThO}_2$ .

**【0061】** When such hard particles are dispersed in a large amount in the raw material powder, even if the raw material powder is finely pulverized, the formability and sinterability of the raw material powder has been remarkably poor conventionally. On the contrarily, in the case of the present invention, even when the hard particles are included in a large amount in the raw material powder, it is possible to produce high-density green compacts. Moreover, when the resulting green compacts are sintered, it is possible to produce high-density sintered bodies by heating the green compacts in a short period of time. In addition, even when the heating time is prolonged in the sintering step in order to sufficiently diffuse the additive elements, the resulting sintered bodies exhibit the dimensional change so less, and are accordingly stable dimensionally.

**【0062】** Hence, when the present invention is used, it is possible to produce high-density green compacts or sintered bodies even if the upper limit proportion of the hard-particle powder in the raw material powder is increased to 5% by mass, 10% by mass, 15% by mass and 20% by mass. Note that the proportion of the hard-particle powder is a proportion when the entire raw material powder after

mixing is taken as 100% by mass.

**【0063】** The alloys, compounds and hard particles included in the raw material powder are not necessary required to keep the powdery shape in the green compacts or the metallic sintered bodies resulting therefrom. They can be turned into more stable states when the raw material powders are made into the green compacts by pressurizing or when the green compacts are made into the metallic sintered bodies by heating. For example, in Ti-based sintered bodies, there is a case where  $\text{TiB}_2$  particles are turned into TiB which is more stable and harder.

**【0064】** The respective powders can be mechanically pulverized powders, hydrogenated-dehydrogenated powders, and atomized powders. Moreover, their production processes do not matter at all. In addition, the raw material powder can be granulated powders. It is not necessarily needed to specify the particle diameters of the raw material powder. However, it is preferred that the average particle diameter can fall in a range of from 1 to 100  $\mu\text{m}$ , for example.

**【0065】** In the present invention, mixing the raw material powder with lubricants is not excluded. When a lubricant is included in a small amount in the raw material powder, it is possible to improve the flowability of the raw material powder. If such is the case, it is more preferable to use the higher fatty acid-based lubricant set forth in the present specification. Note that the higher fatty acid-based lubricant includes those dispersed in a dispersion. However, when the raw material powder is mixed with a large amount of lubricants, it is not preferable because the attainable density of green compacts lowers as described above.

## (2) Higher Fatty Acid-Based Lubricant

**[0066]** The higher fatty acid-based lubricant set forth in the present specification means both lubricants, i.e., lubricants comprising higher fatty acids and lubricants comprising metallic salts of higher fatty acids. The higher fatty acid can be stearic acid, palmitic acid, and oleic acid. The metallic salt of the higher fatty acid can be lithium salts, calcium salts, and zinc salts, for example. Specifically, the metallic salt of the higher fatty acid can be lithium stearate, calcium stearate, zinc stearate, barium stearate, lithium palmitate, lithium oleate, calcium palmitate, and calcium oleate. Note that higher fatty acid-based lubricants whose major component is at least one of the compounds listed above can satisfactorily be the higher fatty acid-based lubricant set forth in the present specification.

**[0067]** The higher fatty acid-based lubricant can preferably be solid in a temperature range of from room temperature to warm temperature. When the higher fatty acid-based lubricant is liquid, it flows downward so that it is difficult to uniformly apply it to the inner surface of the die.

**[0068]** In order to efficiently and uniformly apply the higher fatty acid-based lubricant to the inner surface of the die, the higher fatty acid-based lubricant can preferably be dispersed in a dispersion. The dispersion can comprise water, alcohol-based solvents, or mixture liquids of water and alcohol-based solvents. When the higher fatty acid-based lubricant dispersed in such a dispersion is sprayed onto the die, which is heated, the water and/or the alcohol-based solvents evaporate instantaneously so that it is possible to form a uniform lubricant film with ease. In particular,

when the dispersion is mixed with alcohol-based solvents, the water and the like evaporate so quickly that it is more likely to form a uniform and smooth lubricant film.

**【0069】** In the present invention, active metallic powders are used which are very likely to be seized to dies inherently. Accordingly, it is especially important to form a uniform lubricant film with the higher fatty acid-based lubricant. The uniform lubricant film prolongs the longevity of dies, and makes it possible to stably produce high-density and quality green compacts.

**【0070】** When the die is heated, a suitable die temperature depends on the dispersions. For example, when the dispersion comprises water, the die temperature can preferably be controlled to 100 °C or more. When the dispersion is mixed with alcohol-based solvents, the die temperature can be low temperatures of less than 100 °C depending on the concentration of the alcohol-based solvents. Indeed, it is further preferable to control the die temperature to such temperatures that the compacting step can be carried out in warm states. Anyway, the die temperature can preferably be from the boiling point of the dispersion or more to less than the melting point of the higher fatty acid-based lubricant. The die temperature is controlled to less than the melting point of the higher fatty acid-based lubricant in order to inhibit the higher fatty acid-based lubricant from running downward.

**【0071】** When mixture liquids in which water is mixed with alcohol-based solvents are used as the dispersion, the dispersion can preferably comprise alcohol-based solvents in an amount of from 1 to 50% by volume, further preferably from 5 to 25% by volume, and the balance of water. When the proportion of alcohol-based solvents

is less than 1% by volume, the advantage of mixing alcohol-based solvents is effected less. When the proportion of alcohol-based solvents exceeds 50% by volume, the odors of alcohol-based solvents degrade the working environments, and such a large amount of alcohol-based solvents results in increasing costs involved.

**【0072】** As for such an alcohol-based solvent, it is possible to use methyl alcohol, ethyl alcohol, and isopropyl alcohol. However, as far as alcohol-based solvents exhibit a boiling point lower than that of water, and as far as they are not harmful when they evaporate, their types do not matter at all.

**【0073】** The higher fatty acid-based lubricant dispersed in the dispersion can preferably be formed as powders comprising particles whose maximum particle diameter is 30  $\mu\text{m}$  or less. When particles whose maximum particle diameter exceeds 30  $\mu\text{m}$  are included, the lubricant film formed on the inner surface of the die becomes uneven. Moreover, the particles of the higher fatty acid-based lubricant readily precipitate in the dispersion so that it is difficult to uniformly apply the higher fatty acid-based lubricant to the inner surface of the die.

**【0074】** Moreover, in order to uniformly disperse the higher fatty acid-based lubricant in the dispersion such as water, it is preferable to add a surfactant in the dispersion in advance.

**【0075】** The surfactant can be alkylphenol-based surfactants, 6-grade polyoxyethylene nonyl phenyl ether (EO), 10-grade polyoxyethylene nonyl phenol ether (EO), anionic surfactants, cationic surfactants, amphoteric surfactants, nonionic surfactants and boric acid ester-based emulbon "T-80" (trade name), for example.

**【0076】** One or more of the surfactants can be appropriately selected

to use depending on using higher fatty acid-based lubricants. For example, when lithium stearate (hereinafter abbreviated to as "LiSt") is used as the higher fatty acid-based lubricant, it is preferable to simultaneously add three kinds of surfactants, 6-grade polyoxyethylene nonyl phenyl ether (EO), 10-grade polyoxyethylene nonyl phenyl ether (EO) and boric acid ester emulbon "T-80," to the dispersion at the same time.

**[0077]** The three surfactants are added to the dispersion, because LiSt is less likely to disperse in water or the like when the boric acid ester emulbon "T-80" is added to the dispersion independently. On the other hand, LiSt disperses in water or the like, when the 6-grade polyoxyethylene nonyl phenyl ether (EO) and the 10-grade polyoxyethylene nonyl phenyl ether (EO) are added to the dispersion independently. However, when the resulting dispersions are diluted, the higher fatty acid-based lubricant is less likely to disperse uniformly. Therefore, when LiSt is used as the higher fatty acid-based lubricant, it is preferable to compositely add the three surfactants to the dispersion appropriately. The addition of the surfactant can preferably fall in a range of from 1.5 to 15% by volume when the entire dispersion involving the surfactant is taken as 100% by volume. In this instance, note that it is preferable to mix the three surfactants in a volumetric proportion of 1 : 1 : 1.

**[0078]** The more the addition of the surfactant is, the more the higher fatty acid-based lubricant such as LiSt is dispersed in water or the like. However, when the addition of the surfactant is too much, the viscosity of the resulting dispersions heightens so that it is difficult to finely pulverize the particles of the higher fatty acid-based lubricant by a pulverizing treatment described later.



**【0079】** Moreover, when an antifoaming agent is further added to the dispersion in a small amount appropriately, a uniform lubricant film is likely to form. The antifoaming agent can be silicone-based antifoaming agents, for example. The addition of the antifoaming agent can preferably fall in a range of from 0.1 to 1% by volume approximately when the entire volume of the dispersion is taken as 100% by volume.

**【0080】** When a powdery higher fatty acid-based lubricant is dispersed in the dispersion involving the surfactant, it is preferable to carry out a ball-milling pulverizing treatment. For example, the ball-milling pulverizing treatment can be carried out in the following manner. 10 to 30 g LiSt is added to 100 cm<sup>3</sup> dispersion, and is pulverized with steel balls covered with polytetrafluorethylene. When the treatment is carried out for 50 to 100 hours approximately, LiSt which is pulverized to have the maximum diameter of 30  $\mu$ m or less is dispersed to float in the dispersion.

### (3) Applying Step

**【0081】** When the higher fatty acid-based lubricant is applied to the inner surface of the die, it is preferable to properly dilute the dispersion in which the higher fatty acid-based lubricant is dispersed. Specifically, when the entire diluted dispersion is taken as 100% by mass, the stock dispersion can preferably be diluted so that the concentration of the higher fatty acid-based lubricant such as LiSt is from 0.1 to 5% by mass, further from 0.5 to 2% by mass. When the stock dispersion is thus diluted, it is possible to form thin and uniform lubricant films.

**【0082】** It is possible to uniformly apply the higher fatty acid-based

lubricant to the inner surface of the die by spraying the diluted dispersion with spraying guns for coating operations, for example. Moreover, the higher fatty acid-based lubricant can be applied to the inner surface of the die with electrostatic coating devices such as electrostatic guns. In addition, it is possible to appropriately refer to the methods disclosed in Fig. 1 or Fig. 2 of above-described PCT International Laid-Open Publication No. WO01/43,900 for specific methods for uniformly applying the higher fatty acid-based lubricant to the inner surface of the die.

#### (4) Compacting Step

**【0083】** In the present compacting process, the compacting step is a step in which the active metallic powder which is filled into the die with the higher acid-based lubricant applied is formed by warm pressurizing.

**【0084】** The term, "warm," set forth in the present specification depends on using raw material powders and higher fatty acid-based lubricants. It seems difficult to explicitly define the specific temperatures. If the term, "warm," is defined daringly, it specifies temperature ranges where the advantage of reducing ejection forces are effected even when high-pressure compaction is carried out. However, according to the experiences of the present inventors, such a warm state can be defined by a temperature of an area where at least the inner surface of the die contacts with the raw material powder (hereinafter referred to as a "contact-area temperature"), and the contact-area temperature can desirably fall in a range of from 100 to 225 °C, further desirably from 100 to 180 °C. The contact-area temperature can be optimized for every active metallic powder. For example, the contact-area temperature can

preferably fall in a range of from 130 to 160 °C when the active metallic element is Ti, and can preferably fall in a range of from 100 to 160 °C when the active metallic element is Al.

**【0085】** Such a warm state can be attained by heating at least one of the die and the raw material powder. However, when both of them are heated to an identical temperature substantially, it is possible to produce a more stable warm state.

**【0086】** In the present compacting process, there is no upper limit regarding the compacting pressure. If the range of the compacting pressure is specified daringly, the compacting pressure falls in a range where no dies or forming apparatuses are damaged or broken. Therefore, it is possible to carry out forming powders without problems even by such a high compacting pressure as 2,500 MPa approximately, which has been unconceivable in forming active metallic powders. However, there is a pressure range where not only sufficiently high-density green compacts can be produced but also the productivity can be improved, and the compacting pressure can preferably fall in a range of from 392 to 2,000 MPa, further preferably from 588 to 1,568 MPa. When the compacting pressure is less than the lower limit, 392 MPa, no high-density green compacts can be produced. Note that such compacting pressures do not necessitate to use the present compacting process at all, and lie at the level which even the conventional powder compacting processes can reach. In the present compacting process, the lower limit of the compacting pressure can preferably be 686 MPa or more, further preferably be 784 MPa or more.

**【0087】** The compacting pressure can be optimized for every active metallic powder. For example, the compacting pressure can

preferably fall in a range of from 500 to 2,500 MPa, further preferably from 784 to 1,568 MPa, when the active metallic element is Ti. Moreover, the compacting pressure can preferably fall in a range of from 392 to 2,500 MPa, further preferably from 588 to 1,568 MPa, when the active metallic element is Al.

**【0088】** The relationship between the compacting pressures and the ejection forces will be hereinafter described.

**【0089】** In usual powder compacting, the higher the compacting pressure is, the higher the ejection force is required to eject green compacts from dies. However, in the present compacting process, although it is possible to achieve highly densifying green compacts by enlarging the compacting pressure, the ejection force is hardly changed or is increased slightly. In addition, in accordance with the present compacting process, the ejection force is reduced by a factor of about 1/10 compared with the case where the conventional powder compacting processes are used. For example, the ejection force can be 10 MPa or less in the ejecting step when the compacting pressure is 784 MPa or more in the compacting step. The ejection force does not change even when the compacting pressure is 980 MPa or more, further 1,176 MPa or more, furthermore 1,372 MPa or more. To be more precise, the ejection force can be 5 MPa or less, further 3 MPa or less.

**【0090】** Let us observe the ejection force for every active metallic powder. When the active metallic element is Ti, the ejection force can preferably be 10 MPa or less, further 3 MPa or less, when the compacting pressure is 784 MPa or more. When the active metallic element is Al, the ejection force can preferably be 5 MPa or less when the compacting pressure is 392 MPa or more, and can further

preferably be 1 MPa or less when the compacting pressure is 588 MPa or more.

**【0091】** In the present compacting process, when the pressure ratio, the ratio of the ejection force with respect to the compacting pressure, is examined, the pressure ratio can preferably show a decreasing tendency when the compacting pressure increases.

#### (5) Others

**【0092】** The die set forth in the present specification can be either made of high-speed steel or high-speed tool steel, or can be made of cemented carbide. The inner surface of the die can be subjected to a TiN coating treatment. Note that the smaller the superficial roughness of the die is, the more effectively the frictional force between the die and the green compact is reduced. Accordingly, the resulting green compact is improved in terms of the superficial roughness and dimensional stability.

**【0093】** Since the present green compact and metallic sintered body made by sintering it have a high density which is very close to the true density, they are good in terms of the metallic characteristics such as the strength. Therefore, they can be applied not only to a variety of ordinary component parts but also to structural component parts.

**【0094】** In particular, when the active metallic element is Ti, the green compact and metallic sintered body resulting therefrom according the present invention offer incredible effectiveness. Conventionally, in the fields of aviation, space and military, titanium alloys which are lightweight and exhibit high strength (i.e., which are good in terms of the specific strength) have been used in a large volume. However, titanium alloys haven been hardly

applied to consumer products which are mass-produced generally. In particular, iron or steel materials have been often used in mass-produced exclusive component parts. However, there has been no example in which titanium alloys are applied to the mass-produced exclusive component parts instead of the iron or steel materials. This is because the manufacturing cost has gone up sharply when titanium alloys are used. Thus, titanium alloys are not adequately applied to mass-produced component parts which are required to be low cost. The biggest factor heightening the manufacturing cost is that not only the material cost is expensive but also the secondary working cost is extremely high when the workpieces are worked into the respective component parts. This is because the workpiece shapes of titanium alloys are limited.

**【0095】** On the other hand, when the present compacting process, sintering process and working method are used, it is possible to produce component parts made of titanium alloys, which are lightweight and are good in terms of the strength, without substantially generating the high secondary working cost. Accordingly, it is possible to substitute a variety of mass-produced component parts made of titanium alloys for those conventional ones made of iron or steel materials.

**【0096】** As for such mass-produced component parts, there are automotive component parts which require all sorts of strength, a variety of sporting goods and tools, for example. More specifically, the automotive component parts can be automotive engine component parts such as engine valves, valve retainers, valve lifters, piston pins, valve guides, connecting rods and rocker arms. Moreover, the automotive component parts can be power transmission component

parts such as gears, driving shafts and blocks for CVT (i.e., continuously variable transmission). The sporting goods can representatively be golf clubs such as drivers, irons and putters.

**【0097】** Moreover, when the present compacting process, sintering process or working method is applied to conventional die-forming designing, it is possible to form cylinder-shaped component parts, such as billets for extrusion, piston pins, valve guides, valve retainers, connecting rods, blocks for CVT, irons and putters.

**【0098】** In addition, when the present compacting process, sintering process or working method is applied to advanced forming processes such as CNC (i.e., computer numerically controlled) pressing, it is possible to form engine valves, valve lifters, rocker arms, gears, driving shafts and golf-club heads.

#### EXAMPLES

**【0099】** The present invention will be hereinafter describe in more detail with reference to specific examples.

##### (1) Examples

##### (Raw Material Powder)

**【0100】** Before mixing a raw material powder, five powders were first prepared as follows. A pure titanium powder, a pure aluminum powder, an Al-6%Zn-2%Mg-1.5%Cu alloy powder, an Al<sub>3</sub>V powder and a TiB<sub>2</sub> powder were prepared. The pure titanium powder was produced by WUYI Co., Ltd., and had an average particle diameter of 42 μm. The pure aluminum powder was produced by FUKUDA KINZOKU HAKUHUN Co., Ltd., and had an average particle diameter of 30 μm. The alloy powder was produced by SUMITOMO KEIKINZOKU Co., Ltd., and had an average particle diameter of 35 μm. Note that the unit of the alloy composition is expressed by % by mass (being the same hereinafter).

The  $\text{Al}_3\text{V}$  powder was produced by NIHON DENKO Co., Ltd., and had an average particle diameter of 20  $\mu\text{m}$ . The  $\text{TiB}_2$  powder was produced by NIHON SHINKINZOKU Co., Ltd., and had an average particle diameter of 3.5  $\mu\text{m}$ . Note that the  $\text{TiB}_2$  powder corresponds to the hard-particle powder set forth in the present specification.

**[0101]** Then, the powders were used independently, or were mixed appropriately, thereby preparing active metallic powders having 5 compositions as set forth in Table 1.

(Preparation of Die Wall Lubricant)

**[0102]** As a surfactant, 6-grade polyoxyethylene nonyl phenyl ether (EO), 10-grade polyoxyethylene nonyl phenyl ether (EO) and boric acid ester-based emulbon "T-80" (trade name) were used. The three surfactants were mixed in a ratio of 1 : 1 : 1 by volume, and the resulting mixture surfactant was contained in a proportion of 1.5% by volume in 100% by volume water (i.e., a dispersion). Moreover, an antifoaming agent was added to the dispersion in a proportion of 0.1% by volume. In addition, a lithium stearate (hereinafter abbreviated to as "LiSt") powder was dispersed in an amount of 25 g with respect to the 100 cc water including the mixture surfactant. The LiSt had a melting point of about 225  $^{\circ}\text{C}$ , and had an average particle diameter of 20  $\mu\text{m}$ .

**[0103]** Then, the dispersion was subjected to a fine-pulverizing treatment with a ball-milling pulverizing apparatus provided with polytetrafluorethylene-coated steel balls for 100 hours. The resulting stock solution immediately after the fine-pulverizing treatment was diluted with water and an ethyl alcohol-based solvent. In this instance, water was used in an amount of 14 parts by volume, and the ethyl alcohol-based solvent was used in an amount of 5 parts



by volume, respectively, with respect to 1 parts by volume of the stock solution. Hence, the ethyl alcohol-based solvent was added in an amount of 25% by volume with respect to 100% by volume water. Thus, a die wall lubricant to be applied to the inner surface of a die was prepared.

(Die)

**[0104]** A die was prepared. The die was made of cemented carbide, and had a cylinder-shaped cavity whose size was  $\phi$  23.000  $\pm$  0.005 mm  $\times$  50 mm. Moreover, an upper punch and a lower punch were prepared. The upper and lower punches were made of high-speed steel. The inner surface of the die was subjected to a TiN coating treatment in advance to exhibit a superficial roughness of 0.4Z. In addition, a band heater was wound around the die so that the die could be heated whenever appropriate.

(Compacting)

**[0105]** The die and the respective raw material powders were heated to 150 °C. Note that the raw material powders were heated with an oven (i.e., an electric furnace) in air.

**[0106]** To the inner surface of the die which was heated to 150 °C, the die wall lubricant was sprayed uniformly with a spraying gun at a rate of 1 cm<sup>3</sup>/sec. approximately. Thus, a lubricant film was formed on the inner surface of the die in a thickness of about 1.5  $\mu$ m (i.e., an applying step).

**[0107]** Into the die, the heated raw material powders were filled, respectively (i.e., a filling step). The raw materials were compacted by warm pressurizing while changing the compacting pressure in a range of from 392 to 1,568 MPa appropriately (i.e., a compacting step). Table 1 also summarizes the compacting

pressures in the compacting step.

**[0108]** The upper and lower punches were actuated to eject the formed green compacts from the die, respectively (i.e., an ejecting step). The ejection forces in the ejecting step were also measured.

**[0109]** Moreover, the green compacts comprising the Ti-based powders were sintered in vacuum at 1,300 °C for 4 hours (i.e., a sintering step).

## (2) Comparative Examples

**[0110]** As comparative examples, green compacts were produced with the pure titanium alloy and pure aluminum alloy and by compacting them at room temperature. In this instance, a commercially available dry fluorine lubricant "YUNON-S" (trade name) was used as a die wall lubricant, and was applied to the inner surface of the die by spraying in the same manner as the examples. The compacting pressure was controlled basically in such a range that the die was not damaged by galling and the like. Table 1 also summarizes the compacting pressures in the compacting operation.

## (3) Measurements

**[0111]** The green compacts produced in the examples and comparative examples were examined for the green density and the ejection force, respectively. Table 1 also summarizes the results of the measurements. Moreover, Table 1 also summarizes the ratio (i.e., the relative density) of the green density with respect to the true density. Note that the true density was found by examining cast products, which had the same composition as those of the respective raw material powders, for the density. The green density was calculated from measured values which were obtained by measuring the weight and dimensions of the respective green compacts.

**【0112】** The ejection force was determined in the following manner. An ejecting load was measured with a load cell. The measured load was divided by the lateral area of the respective green compacts to determine the ejection force.

**【0113】** Moreover, regarding the metallic sintered bodies, the dimensional change occurred in the sintering step was determined by measuring the dimensions before and after the sintering step. The sintered-body density of the respective sintered bodies was measured by an Archimedes method.

#### (4) Assessment

##### (A) Examples Made of Titanium-based Raw Material Powder

##### (Examples Made of Pure Titanium Powder)

**【0114】** The lines of Table 1 designated with Sample Nos. 1-1 through 1-6 and Sample Nos. C1-1 through C1-3 as well as Figs. 1 through 4 set forth the characteristics when the pure titanium powder was compacted by a variety of compacting pressures.

**【0115】** It is apparent from Table 1 and Figs. 1 through 4 that, in accordance with the present examples in which the pure titanium powder was warm compacted, high-pressure compaction was realized in which the pure titanium powder could be formed by a compacting pressure beyond 1,500 MPa. Thus, it was possible to provide a process for compacting an exceptionally high-density green compact.

**【0116】** Specifically, the green relative density was well over 85%, the conventional maximum level, and reached in a range of from 98 to 99%. Thus, green compacts were produced whose green density was virtually equal to the true density.

**【0117】** Note that the relative density is employed as an index of the green density in Table 1 as well as Fig. 1 and so on, because

the true density depends on the composition. Thus, the relative density is employed in order to objectively assess the extent of high densification by the present compacting process. The discussion is similarly applicable to the sintered-body density.

**[0118]** When observing Fig. 2, it is apparent that, in the examples, the compacting pressure increased remarkably though the ejection force hardly varied. Moreover, when the compacting pressure was about to exceed 600 MPa, the ejection force decreased to such very low values as 5 MPa or less. In addition, when the compacting pressure exceeded 784 MPa, the ejection force was substantially constant at such an extremely low value as about 2.5 MPa.

**[0119]** On the other hand, in room-temperature compacted green-compacts of the comparative examples, galling occurred to the die when the compacting pressure was no more than 588 MPa. Moreover, the relative density of the produced green compacts did not reach even 85% at best. In addition, when the pure titanium powder was compacted at room temperature, the ejection force enlarged sharply in proportion to the increment of the compacting pressure substantially.

**[0120]** When observing Fig. 3, it is seen that the green density increased as the compacting pressure increased, and that the sintered-body density increased as the green density increased. In particular, in the present examples, when the green compacts which were compacted by the compacting pressure of 1,176 MPa or more were sintered, the density of the resulting sintered body increased virtually equal to the true density.

**[0121]** In addition, when observing Fig. 4, it is understood that the dimensional change before and after sintering was very small

in the present examples so that it fell in a range of from about 1 to 3%. On the other hand, the comparative examples in which the pure titanium powder was compacted at room temperature, the original green compacts per se had a low density. Accordingly, the dimensional change before and after sintering was considerably large so that it fell in a range of from 4 to 10%.

(Examples Made of Titanium Alloy Powder)

**【0122】** The lines of Table 1 designated with Sample Nos. 2-1 through 2-3 and Sample Nos. 3-1 through 3-3 as well as Figs. 5 through 7 set forth the characteristics when the alloy mixture powder as well as the alloy mixture powder with the  $\text{TiB}_2$  powder mixed were compacted by a variety of compacting pressures. Note that the alloy mixture powder was prepared by mixing the pure titanium powder with the  $\text{Al}_3\text{V}$  powder.

**【0123】** First, when the mixture powder whose alloy composition was Ti-6Al-4V was warm compacted, green compacts and metallic sintered bodies were produced whose green density and sintered body density were exceptionally high. In particular, the sintered body density stabilized at such a high value that the relative density was about 99.5% in all of Sample Nos. 2-1 through 2-3. Moreover, in Sample Nos. 2-1 through 2-3, the ejection force stabilized at such a low value that it was about 1 MPa or less.

**【0124】** Then, when the alloy mixture powder with the  $\text{TiB}_2$  powder mixed was compacted by warm pressurizing, the resulting green compacts and metallic sintered bodies had a sufficiently large green density and sintered body density, and were ejected from the die by an adequately small ejection force. For example, when the compacting pressure was 1,176 MPa, the relative density of the green

compact reached 94%, and the sintered-body density of the metallic sintered body arrived even at 99%. In this instance, the ejection force of the green compact was about 5 MPa or less in all of Sample Nos. 3-1 through 3-3.

**【0125】** Moreover, when the  $\text{TiB}_2$  powder was mixed in an amount of 6% by mass, it is understood from Fig. 6 that an unusual phenomenon occurred that the ejection force decreased despite the enlarging compacting pressure.

**【0126】** However, when Sample Nos. 3-1 through 3-3, in which the  $\text{TiB}_2$  powder was mixed, were compared with Sample Nos. 2-1 and 2-3 free from the  $\text{TiB}_2$  powder, the densities were lower slightly and the ejection forces were somewhat higher for identical pressures. However, it seems that the density decrement and ejection force increment depend on the mixing amount of the  $\text{TiB}_2$  powder. It is needless to say that all of the density and ejection-force values are remarkably good compared with the case where the alloy mixture powder with the  $\text{TiB}_2$  powder mixed was compacted at room temperature.

**【0127】** Moreover, it is understood from Fig. 7 that all of Sample Nos. 2-1 through 2-3 and Sample Nos. 3-1 through 3-3 according to the present examples had a higher density than comparative samples did. Note that, in the comparative samples, the alloy mixture powder with the  $\text{TiB}_2$  powder mixed was compacted by 392 MPa by means of CIP.

(B) Examples Made of Aluminum-based Raw Material Powder

(Examples Made of Pure Aluminum Powder)

**【0128】** The lines of Table 1 designated with Sample Nos. 4-1 through 4-7 and Sample Nos. C2-1 through C2-3 as well as Figs. 8 and 9 set forth the characteristics when the pure aluminum powder was

compacted by a variety of compacting pressures.

**【0129】** The overall tendency of the characteristics was similar to Sample Nos. 1-1 through 1-6 in which the pure titanium powder was warm compacted. The green compacts according to the present examples had an extremely high density.

**【0130】** However, in Sample Nos. 4-1 through 4-7 according to the present examples, the ejection force was so low as about 1 MPa or less regardless of the compacting pressures. Namely, even when the compacting pressure was low, for example, when it was 392 MPa in Sample No. 4-1, the ejection force was low. When observing the column of Table 1, "Outside Dia. after Ejection," it is understood that the phenomenon seems to have resulted from the fact that the outside diameter of the ejected green compacts was as large as or slightly less than the inside diameter of the die. However, as can be seen from Table 1 and Fig. 9, no such tendency was not observed in Sample Nos. C2-1 through C2-3 in which the pure aluminum powder was compacted at room temperature.

(Examples Made of Aluminum Alloy Powder)

**【0131】** The lines of Table 1 designated with Sample Nos. 5-1 through 5-3 as well as Figs. 10 and 11 set forth the characteristics when the one and only aluminum alloy powder whose alloy composition was Al-6Zn-2Mg-1.5Cu was compacted by a variety of compacting pressures. The overall tendency of the characteristics was similar to Sample Nos. 4-1 through 4-7 in which the pure aluminum powder was warm compacted.

**【0132】** However, compared with Sample Nos. 4-1 through 4-7 in which the pure aluminum powder was warm compacted, the density of the resulting green compacts was lower slightly and the ejection forces

were higher slightly for identical compacting pressures when the aluminum alloy powder was warm compacted. It seems that this phenomenon resulted from the fact that the aluminum alloy powder comprised particles which exhibited higher strength than the pure aluminum particles did so that the compressibility lowered. Regardless of the phenomenon, the relative density of the green compact reached 94% or more. Accordingly, it is understood that fully high-density green compacts could be produced. It is needless to say that all of the density and ejection-force values are remarkably good compared with the case where the aluminum alloy powder was compacted at room temperature.

#### (C) Metallic-Sintered Body

##### Made of

##### Raw Material Powder with Increased Hard-Particle Content

**[0133]** The larger the  $TiB_2$ -powder content is, the resulting metallic sintered bodies can exhibit higher rigidity and strength. On the other hand, the larger the  $TiB_2$ -powder content is, the more the formability and sinterability of green compacts lowers in general. Accordingly, in order to further assess the formability and sinterability according to the present compacting process and sintering process, a metallic sintered body was newly produced whose  $TiB_2$ -powder content was increased up to 12% by mass.

**[0134]** Except the  $TiB_2$ -powder content, a new sample, another example according to the present invention, was produced under the same conditions as those of Sample No. 3-3. Specifically, the titanium alloy mixture powder with the  $TiB_2$  powder mixed was compacted with the die which was heated to 150 °C by a compacting pressure of 1,568 MPa, and thereafter the resulting green compact was sintered at



1,300 °C. Moreover, a comparative sample was produced in the following manner. A raw material powder having the same composition as that of the new sample was compacted by a compacting pressure of 588 MPa at room temperature in the above-described manner, and thereafter the resulting green compact was sintered at 1,300 °C.

**[0135]** Figs. 12 and 13 illustrate how the relative density and dimensional change of the present sample and comparative sample changed when the sintering time was varied, respectively. Note that the hard-particle content is expressed by 20% by volume TiB in the drawings, because the 12% by mass TiB<sub>2</sub> was turned into 20% by volume TiB by sintering.

**[0136]** First, as can be seen from Fig. 12, in the present sample, a sufficiently high-density green compacts were produced by sintering the raw material powder in an extremely short period of time, and the relative densities were close to 100%. On the other hand, in the comparative sample, it took a longer time to sinter the raw material powder in order to heighten the relative density of the resulting metallic sintered bodies. Note that, even when the raw material powder is pulverized to disperse a large amount of hard particles in the raw material powder, the conventional process like the comparative sample is considerably poor in terms of the powder formability and sinterability, and accordingly cannot produce metallic sintered bodies whose density is as high as those of the metallic sintered bodies produced by the present sample.

**[0137]** Then, as can be understood from Fig. 13, in the present sample, the dimensional change was very small, i.e., 2% approximately, and stabilized thereat. On the other hand, in the comparative sample, the dimensional change decreased greatly as the sintering time

prolonged, and did not stabilize at all.

**【0138】** Thus, in accordance with the present sample, it became evident that metallic sintered bodies can be produced which have a high density and are good in terms of the dimensional stability.

#### (D) Mechanical Characteristics

of

##### Metallic Sintered Body with Hard Particles Dispersed

**【0139】** A raw material powder including a  $\text{TiB}_2$  powder was compacted by pressuring, and was further sintered to produce a metallic-sintered-body sample. The resulting sample was examined for the tensile strength and fatigue strength.

**【0140】** The composition of the used raw material powder was the same as that of Sample No. 3-3 recited in Table 1. The present sample was produced in the same manner as Sample No. 3-3. However, the present sample was formed as a shape of traverse test pieces whose size was 10 mm  $\times$  10 mm  $\times$  55 mm. A comparative sample was made by sintering a green compact, which was compacted as the identical shape by 392 MPa by means of CIP, at 1,300 °C. The comparative sample which was sintered for 4 hours was labeled as Comparative Example No. 1. The comparative sample which was sintered for 16 hours was labeled as Comparative Example No. 2. The resulting samples were processed into a tensile-test test piece and a rotating bending fatigue-test test piece. The respective test pieces were examined for the mechanical characteristics. Figs. 14 and 15 illustrate the result of the examinations. For reference, the hard-particle content is expressed by 10% by volume TiB in the drawings, because the 6% by mass  $\text{TiB}_2$  was turned into 10% by volume TiB by sintering.

**【0141】** The following are apparent from Figs. 14 and 15. The

metallic sintered bodies of the present sample had an exceptionally higher sintered-body relative density than those of Comparative Example Nos. 1 and 2. Moreover, it was verified that the metallic sintered bodies of the present sample were remarkably better than those of Comparative Example Nos. 1 and 2 in terms of all of the tensile strength, elongation and fatigue strength

(E) Results of Superficial Analysis

on

Green Compacts according to the Present Invention

**[0142]** The surface of the green compacts of Sample Nos. 1-4 and 4-5 recited in Table 1 was analyzed by TOF-SIMS, respectively. Note that the green compact of Sample No. 1-4 was made of the pure titanium powder, and the green compact of Sample No. 4-5 was made of the pure aluminum powder. Figs. 16 and 17 illustrates secondary ion images produced as a result of the analysis.

**[0143]** From the drawings, it was confirmed that, for both of Sample Nos. 1-4 and 4-5, the distribution of stearic acid resembled the distribution of Ti or Al rather than the distribution of Li. It seems that the result suggests that a mechanochemical reaction occurred to form a new metallic soap film, which are believed to be titanium stearate or aluminum stearate, on the surface of the green compacts in the compacting step according to the present examples.

**[0144]** Having now fully described the present invention, it will be apparent to one of ordinary skill in the art that many changes and modifications can be made thereto without departing from the spirit or scope of the present invention as set forth herein including the appended claims.

TABLE 1

Sample No.		Composition (% by mass)	Compaction Pressure (MPa)	Ejection Force (MPa)	Green Compact		Metallic Sintered Body				Note	
					Green-compact Density (g/cm <sup>3</sup> )	Relative Density (%)	Outside Dia. after Ejection (mm)	Sintered- body Density (g/cm <sup>3</sup> )	Relative Density (%)	Dimension Change before and after Sintering (%)		
Ex.	1-1	Pure Ti	588	3.5	4.025	89.2	23.059	4.325	95.9	-2.60		
	1-2		784	1.9	4.193	93.0	23.061	4.384	97.2	-1.59		
	1-3		980	2.4	4.292	95.2	23.065	4.451	98.7	1.37		
	1-4		1176	2.5	4.364	96.8	23.070	4.496	99.7	-1.11		
	1-5		1372	2.6	4.391	97.4	23.075	4.501	99.8	-0.87		
	1-6		1568	2.2	4.422	98.0	23.079	4.505	99.9	-0.60		
	2-1	Ti-6Al-4V	784	0.9	3.991	91.1	23.065	4.403	99.3	-3.26	Mixture Powder of Pure Ti Powder and Alloy Powder	
	2-2		1176	0.5	4.201	95.9	23.071	4.407	99.4	-1.61		
	2-3		1568	0.5	4.285	97.8	23.081	4.412	99.5	-0.96		
	3-1	Ti-6Al-4V +6TiB <sub>2</sub>	784	5.1	3.956	90.2	23.072	4.332	97.4	-3.04	Mixture Powder of said Mixture Powder and Hard-particle Powder TiB <sub>2</sub> : 6% by mass	
	3-2		1176	3.6	4.143	94.3	23.078	4.395	98.8	-2.06		
	3-3		1568	2.7	4.234	96.5	23.083	4.412	99.2	-1.46		
	4-1	Pure Al	392	0.3	2.613	96.8	22.997	-	-	-		
	4-2		588	0.7	2.656	98.4	22.992	-	-	-		
	4-3		784	0.7	2.672	99.0	22.994	-	-	-		
	4-4		980	0.7	2.682	99.4	22.994	-	-	-		
	4-5		1176	0.8	2.686	99.5	22.993	-	-	-		
	4-6		1372	0.8	2.667	99.8	22.994	-	-	-		
	4-7		1568	0.5	2.667	99.8	22.995	-	-	-		
	5-1	Al-6Zn-2Mg-1.5Cu	588	1.3	2.616	93.4	23.014	-	-	-	Equivalent to JIS A7475	
	5-2		980	1.1	2.741	97.9	23.029	-	-	-		
	5-3		1568	1.4	2.794	99.8	23.038	-	-	-		
	Comp. Ex.	C1-1	Pure Ti	294	8.0	3.209	71.2	23.068	4.235	93.9	-9.58	Room-temp. Compaction
		C1-2		441	16.3	3.521	78.1	23.075	4.290	95.1	-6.94	
C1-3		588		24.1	3.728	82.9	23.082	4.300	95.3	-4.95		
C2-1		Pure Al	392	4.1	2.583	95.7	23.056	-	-	-	Room-temp Compaction	
C2-2			588	5.7	2.615	96.9	23.057	-	-	-		
C2-3			784	6.5	2.640	97.8	23.059	-	-	-		